Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater?

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[1] Widespread pollution of groundwater by nutrients due to 20th century agricultural intensification has been of major concern in the developed world for several decades. This paper considers the River Thames catchment (UK), where water-quality monitoring at Hampton (just upstream of London) has produced continuous records for nitrate for the last 140 years, the longest continuous record of water chemistry anywhere in the world. For the same period, data are available to characterize changes in both land use and land management at an annual scale. A modeling approach is used that combines two elements: an estimate of nitrate available for leaching due to land use and land management; and, an algorithm to route this leachable nitrate through to surface or groundwaters. Prior to agricultural intensification at the start of World War II, annual average inputs were around 50 kg ha^{-1}, and river concentrations were stable at 1 to 2 mg l^{-1}, suggesting in-stream denitrification capable of removing 35 (±15) kt N yr^{-1}. Postintensification data suggest an accumulation of 100 (±40) kt N yr^{-1} in the catchment, most of which is stored in the aquifer. This build up of reactive N species within the catchments means that restoration of surface nitrate concentrations typical of the preintensification period would require massive basin-wide changes in land use and management that would compromise food security and take decades to be effective. Policy solutions need to embrace long-term management strategies as an urgent priority.

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1. Introduction

[2] The world faces an ever more challenging dilemma: feed a rapidly growing population and simultaneously provide safe and secure supplies of drinking water, and maintain ecosystem quality. Crop yields increased after 1940 because of the mechanization of agriculture in the developed world; this has secured food supplies and guarded against famine [*Cooke*, 1976]. But increased food production has caused soil erosion [*Boardman and Vandaele*, 2010] and pollution of surface and groundwaters [*Burt et al.*, 1993]. These continue to affect human health and livelihoods, and the health and quality of freshwater and marine ecosystems. A particular problem has been the eutrophication of surface and marine waters because of nutrient enrichment [*Burt et al.* 2011a, *Paces*, 1982; *Turner and Rabalais*, 1991; *Reynolds and Descy*, 1996; *Rabalais*, 2002; *Mayer et al.* 2002; *Holman et al.*, 2008, 2010; *Howden et al.*, 2009; *Weatherhead and Howden*, 2009]. Such consequences of modern agriculture have been recognized in recent years and attempts made to reduce impacts through improved farming practices and legislative controls (e.g., the development of nitrate sensitive areas across the EU [*Worrall et al.*, 2009a]).

[3] There are, however, considerable technical and practical challenges for scientists, engineers, resource managers, and policymakers in both understanding and controlling these externalities of modern agriculture if we are to maintain present and future food and water security. A key challenge is to understand the timescales over which solutes are transported from the land, through soil, vadose, and phreatic zones to discharge into boreholes, springs, or as river base flow [*Howden et al.*, 2011b], and thereby deliver effective methods to maintain and increase food production, and reduce diffuse pollution of agrichemicals to water resources.

[4] The science of catchment hydrology is still young; many fundamental (and some yet unasked) questions remain to be answered in respect of how water moves through the environment and how land use links through to water quality [*McDonnell et al.*, 2010]. It is increasingly clear that catchment hydrological responses integrate a spectrum of contributions over a range of temporal and spatial scales [e.g., *van der Velde et al.*, 2010; *Sivapalan*, 2003a]; a catchment simultaneously integrates spatial responses from fields and small watersheds, and a range of flow paths each with their own residence times [*Sivapalan*, 2003b; *Burt and Pinay*, 2005]. Thus, a detailed process description of how agricultural land use and management connects through to drinking water quality in groundwater and rivers requires the integration of soil science, catchment hydrology, hydrogeology,

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and landscape and freshwater ecology to a level that we are unable to achieve given present knowledge and data availability. Given the requirement to achieve good ecological status for surface and groundwater systems (e.g., via the European Union's [EU] Water Framework Directive), the downstream impact of agrichemicals on freshwater ecology are of particular importance but are rarely considered.

[5] The challenge to understand the downstream effect of particular agrichemicals (e.g., inorganic nitrate or phosphate fertilizer) on water resources, is set because we still lack a thorough understanding of: the limiting nutrients (macro and micro) for aquatic ecosystems [*Tilman et al.*, 1982; *Rabalais*, 2002; *Howarth and Marino*, 2006]; how other pollutants affect these systems [*Cloern*, 2001]; how resilient the freshwater systems are [*Mulholland et al.*, 2006]; whether past changes are irreversible [*Odum*, 1983]; and, what the long-term prognosis for ecosystem health and biodiversity might be [*Carpenter et al.*, 1998]. For water resources in groundwater systems, from individual aquifers to groundwater-dominated river basins, pollution from diffuse land-based sources is an even greater challenge for water resource managers, scientists, and policymakers alike, because:

[6] 1. The physical processes that control recharge, unsaturated, and saturated zone flow, are complex and highly influenced by heterogeneity at all scales [*Mathias*, 2005].

[7] 2. Mechanisms that control rates of solute transport through soils and aquifers add another layer of complexity [*Barraclough et al.*, 1994].

[8] 3. Transit times between the land surface and the groundwater discharge point (whether it is an abstraction well, spring, or diffuse input to the river) can vary over several orders of magnitude from hours to millennia [*Jackson et al.*, 2006].

[9] 4. When the above points (1–3) are coupled, it becomes very difficult to identify how specific agricultural practices influence groundwater quality at those places where clean water resources are needed.

[10] Notwithstanding this complexity, several questions must be answered to achieve a sustainable level of land use and management (i.e., food production) such that groundwater quality, and the health of downstream freshwater and terrestrial ecosystems, is maintained. Specifically, for the case of nitrate in ground- and surface waters, the first concerns are what level of nitrogen input to agricultural land should be permitted such that impacts on surface and groundwater quality can remain sustainable in the long term [*Carpenter et al.*, 1998]. Nitrate is both an important nutrient and a tracer for other nutrients, elements, and pollutants moving through aquifers [*Burt et al.*, 1993] and there is increasing evidence of long residence-time flow paths, even in shallow groundwater systems [*Jackson et al.*, 2006]. In this context, short water-quality records raise more questions than they answer [*Burt et al.*, 2008]: long records are needed to reduce uncertainty and allow questions of long-term change to be addressed [*Burt*, 1994, *Burt et al.*, 2011b; *Howden et al.*, 2011a]. Central to the management of groundwater resources are the key travel time distributions that link inputs to land and solute transport through to rivers receiving runoff and base flow [*Jackson et al.*, 2006]: How can these be modeled in a way that balances issues of complexity and parsimony? There is then the question of what historic data, if any, are available to characterize inputs and outputs over recent decades, given the likely response times of groundwater systems [*Davis et al.*, 1979; *Howden et al.*, 2011b]. Further, we need to estimate the capacity of a catchment system to remove or attenuate nutrient export, including the roles of riparian buffer zones [*Burt et al.*, 2010] and in-stream losses both in the river and in marine waters [*Seitzinger et al.*, 2002; *Boyer et al.*, 2006]. Our approach here is to construct a relatively simple model that works at the scale of interest and incorporates the important elements of historical loading and catchment response.

[11] This paper presents a study of nitrate transfer from agricultural land through water resources in the River Thames (UK), a basin where water supplies for ~5 million people are obtained from aquifers, and a drinking water for a further 6 million (i.e., London) is taken directly from the river [*Whitehead*, 1990]. The Thames has a history typical of river basins in the developed world affected by modern, intensive food production in the twentieth century. The continuous monthly record of average nitrate concentrations for the Thames at Hampton (just upstream of London) for 140 years, starting in 1868 (Figure 1), is the longest continuous record of water chemistry available anywhere in the world [*Howden et al.*, 2010]. In 1867, the British Government also began the national agricultural census, which collected details of land use (numbers of animals, areas of particular crops, etc.) for each calendar year; Thus, we use 140-yr records of both land use and river response for the Thames catchment upstream of London.

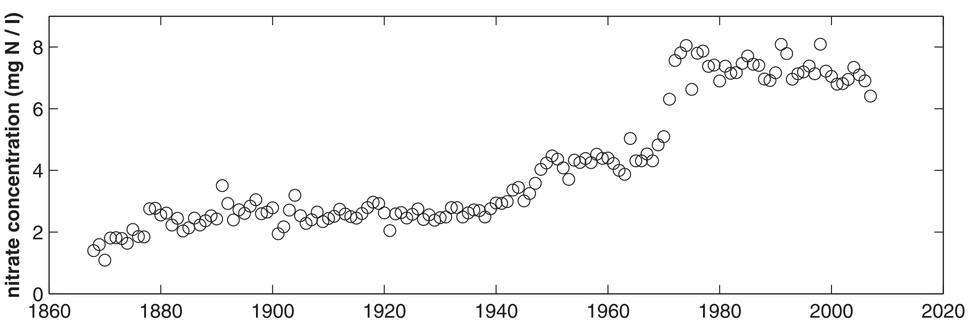

Figure 1. The annual average nitrate concentrations in the Thames north of London at Hampton, from 1868 to 2008. The annual averages calculated for calendar years from reported monthly averages based on weekday samples taken at the inlet of the Hampton water treatment works.

Specifically, given the importance of agricultural land use/management for food supply and ground- and surface-water abstraction for water supply in the Thames basin, can we identify how land use and management practices are linked through to surface and groundwater quality in the long-term and thereby determine whether past and current land use and management practices lead to a sustainable groundwater resource; how we can approximate what a sustainable regime might comprise; and, how these historical records can inform groundwater resource planning and protection in decades to come.

2. Watershed, Data, and Methods

2.1. The Thames Basin

[12] The Thames basin upstream of London covers an area of $\sim$10,000 km^2. The River Thames is the second longest river in the UK and flows from headwaters in Gloucestershire at $\sim$300 m above ordinance datum (AOD) to the tidal limit at Teddington; major tributaries include the Cherwell, Thame, Kennet, Loddon, Colne, Wey, and Mole. The Thames basin is underlain by a combination of limestone, cretaceous chalk, mudstones, sandstones, and Oxford clay. The hydrogeological characteristics of these formations aggregated for the whole basin are classified by the National River Flow Archive (NRFA: available at http://www.ceh.ac.uk/data/nrfa/data/spatial.html?39001) as, high permeability bedrock (43%); moderate permeability bedrock (10%); low permeability bedrock (37%); generally high permeability superficial deposits (14%); generally low permeability superficial deposits (7%); and mixed permeability superficial deposits (7%). The Thames watershed is predominantly rural with main urban centers in Oxford, Thame, Aylesbury, and Swindon. The main agricultural land uses include nonirrigated arable land (47%), discontinuous urban fabric (16%), pastures (12%), broad-leaved forest (8%), other agricultural areas (4%), and complex cultivation patterns (3%).

[13] Average rainfall for the catchment at Oxford, which lies at the center of the Thames basin, is 645 mm (1767–2008, standard deviation 113 mm). The Thames basin response integrates a range of different river and watershed regimes, from highly responsive rivers (urbanized and low-permeability watersheds) to slow responding groundwater-dominated watersheds. Overall, the NRFA lists the Thames hydrograph at Kingston as being dominated by groundwater responses (65%), with runoff contributing the additional 35%.

2.2. Data

[14] The following data were used:

[15] 1. Land use data: We obtained land-use data for the years 1875–1988 from parish records held at the National Archives at Kew Gardens, London. Access to parish summaries post-1988 is currently restricted, so we reconstructed data from 1988 to 2007 from national land use data based on a correlation between Thames and UK data between 1952 and 1988. The annual data were produced for the following: the total area of land used for agriculture; total land area used for growing arable crops; total land area designated as permanent grassland; total land area designated as temporary grassland; and, total numbers of cattle, sheep, pigs, horses, and poultry.

[16] 2. Land management data: We used data published from national-scale UK studies (see Table 1) to estimate nitrate inputs to the watershed, and uptake of nitrate because of the growth of crops or grass, as described below.

[17] 3. Population data. We used the census returns from 1861 to 2001 (and an Office of National Statistics [ONS] estimate for 2007) to estimate the basin population to estimate sewage effluent contributions to observed fluvial nitrate concentrations.

[18] 4. River flow data: We used mean daily flow data from Kingston, the closest measurements to the chemical

Table 1. Parameters Used in the N-Loading Model

Model Component	Loading (kg N ha^{-1} yr^{-1})	± (%)	Source and Rationale
Livestock			
Cattle	85.7	10	Data from *Addiscott* [1991], verified in experiments reported by Smith (2003). Values are national averages and relate to a mixed-size herd.
Sheep	6.9		
Horses	85.7		
Pigs	8.8		
Poultry	0.44		
Fertilizer[a]			
Arable	see Figure 3	10	Data pre-1971 from *Mittikalli and Richards* [1996]; figures from 1971 from the British Survey of Fertilizer practice [*DEFRA*, 2009]
Grassland			
Grassland plowing			
N released	3973	10	Data from *Whitmore et al.* [1992]
Decay constant	0.125		
Others			
Fixation	28	10	Data from *MAFF* [1977]
Atmospheric deposition			
Pre-1920	4.5	10	Data from *Royal Society* [1983]
Post-1969	16	25	
Crop uptake			
Maximum uptake	150	10	Data approximated from a range of crop yield curves [*Addiscott et al.*, 1991; *Glendining et al.*, 1997; *Macdonald et al.*, 2002; *Stockle and Debaeke*, 1997]
Minimum uptake	50		
Initial uptake rate control	80		

[a]Fertilizer inputs are assumed to be subject to a loss of 12% to 18% because of denitrification [*Royal Society*, 1983].

sampling site. These were available from 1883 to the present (see NRFA, reference 39001).

[19] 5. River nitrate concentrations: We used monthly average nitrate concentrations measured at Hampton between 1868 and 2008 [see *Howden et al.*, 2010] to calculate annual average concentrations.

[20] The nitrate concentration data was listed in archives of the various companies that supplied drinking water to London between 1868 and 2008. Over the 140 years, samples of raw Thames water were taken each weekday and summarized as monthly averages. In the late 19th century, there were five companies abstracting raw water and, therefore, there are five replicates for each monthly average; these show broad agreement, and were independently verified [*Hamlin*, 1990]. Changes in analytical methods occurred between 1868 and 2008, but none of these caused inhomogeneity in the nitrate record: the observed shifts in concentration modeled here did not coincide with changes in measurement technique.

3. Methods

[21] The model is structured in two parts: an accounting procedure to estimate nitrate available for leaching from the soil, after *Howden et al.* [2011b]; and, a model that uses a two-reservoir transfer-function to route the estimated loading through a runoff and a groundwater pathway.

3.1. Nitrogen Available for Leaching

[22] The nitrate available for leaching from the soil, L (kg ha^{-1} yr^{-1}), was calculated from the following mass balance of estimated annual inputs and outputs due to agricultural land use:

$$L = [I_{\mathrm{atm}} + I_{\mathrm{fix}} + I_{\mathrm{fert}} + I_{\mathrm{animals}} + I_m] - [U_{\mathrm{crops}} + U_{\mathrm{grass}}], \quad (1)$$

where I_x are loading components due to inputs from atmospheric deposition (atm), biological fixation (fix), fertiliser inputs (fert), animal excretion (animals), and enhanced mineralization (m) due to plowing of permanent grassland. U_x are components that remove nitrate from the soil due to uptake by arable crops (crops) and the creation of grassland (grass), respectively (all in units of kg ha^{-1} yr^{-1}).

[23] Inputs, from atmospheric deposition and biological fixation, were taken from regional-scale figures compiled by the *Royal Society* [1983]. Inorganic N-fertilizer inputs prior to 1970 were estimated using data from *Mittikalli and Richards* [1996]; values for missing years were estimated by linear interpolation. Post-1970 data were obtained from the British Survey of Fertiliser Practice (*Department for Environment Food and Rural Affairs (DEFRA)* [2009], Table B2.1). The loading from fertilizers was then estimated from:

$$I_{\mathrm{fert}} = I_{\mathrm{arable}} f_{\mathrm{arable}} + I_{\mathrm{grass}} f_{\mathrm{grass}}, \quad (2)$$

where I_{arable}, I_{grass}, f_{arable}, and f_{grass}, were the average fertilizer application rates (kg N ha^{-1} yr^{-1}) and fractions of the catchment used for arable crops and grassland, respectively. Loading from animals was estimated from:

$$I_{\mathrm{animals}} = \frac{1}{A}\sum_{i=1}^{5} N_i E_i, \quad (3)$$

where N was the number of animals of type i in the catchment, E_i was the excretion rate per animal (kg N ha^{-1} yr^{-1}: see Table 1) and A was the total agricultural catchment area (ha).

[24] The availability of nitrate for leaching due to plowing of permanent pasture was estimated using the approach outlined by *Whitmore et al.* [1992] thus:

$$M_t = M_{\mathrm{arable}} + (M_{\mathrm{grass}} - M_{\mathrm{arable}}) \exp[-kt], \quad (4)$$

where M_t is the mass (kg N ha^{-1}) t years after plowing; M_{arable} is the equilibrium mass of N under the arable regime; M_{grass} is the equilibrium mass of N under the permanent grassland regime; and k is a first-order rate constant. The decrease in M_t over time is assumed to result from the mineralization of organic N (and subsequent loss via crop uptake, volatilization of ammonia, denitrification, and leaching). Mineralization is described by:

$$I_m = M_t(1 - \exp[-kt]). \quad (5)$$

I_m is, therefore, calculated from a combination of newly plowed permanent pasture and the decrease in M_t over time for the areas plowed in previous years (see Table 1 for parameter values).

[25] Nitrogen uptake by arable crops (kg N ha^{-1} yr^{-1}) was calculated from:

$$U_{\mathrm{crops}} = U_{\mathrm{min}} + \frac{[U_{\mathrm{max}} - U_{\mathrm{min}}] I_{\mathrm{total}}}{K + I_{\mathrm{total}}}, \quad (6)$$

where U_{max} and U_{min} are the maximum and minimum crop uptake rates, I_{total} was the total nitrate input from fertilizers, animals, atmospheric deposition, fixation, and enhanced mineralization and, K is a constant that controls the initial rate of increase in U_{crops} for an increase in I_{total}. Parameters were approximated using a range of arable crops typical to the catchment (see Table 1).

[26] In the absence of regular monitoring data, atmospheric deposition was assumed to increase linearly between 1920 and 1970, remaining constant before and after those dates. Consistent atmospheric deposition records for the UK have only been maintained since 1986, but the reported fluxes [*Fowler et al.*, 2005] for wet and dry deposition of both reduced and oxidized forms of nitrogen are incomplete. So we extended the record of dry deposition by linear interpolation of the ratio of wet to dry deposition in those years where both were reported. *Fowler et al.* [2005] only give records to 2001 but further records are available from the Centre for Ecology and Hydrology (CEH: available at www.ceh.ac.uk) for 2004–2006. In order to get flux estimates for 2002 and 2003, linear interpolation was used. It was assumed that inputs from biological fixation were similar to those for the counties of Oxfordshire and Berkshire (which form part of the Thames basin), in the mid 1970s, were in the range 26–30 kg N ha^{-1} yr^{-1} [*Ministry of Agriculture Fisheries and Food* (*MAFF*), 1977]. It was assumed that 12%–18% of soil inorganic N would be lost via denitrification to N_2O [*Royal Society*, 1983].

[27] Population figures are available for every English county at 10-yr intervals from 1841, with additional projected

numbers from 2001 to 2007 (available at http://www.ons.gov.uk). Linear interpolation was used between census years to estimate the population for each year of the study. Values were rescaled to account for the area of each county within the Thames basin. Each population total was multiplied by the annual N excretion rate for humans (2.14 kg per capita per year [*Burt et al.*, 1996]) of which 60% is assumed to be in the form of nitrate [*Worrall and Burt*, 2001]. It is also assumed that all sewage receives primary and secondary treatment. We assumed no net trans-watershed transfers of nitrogen, for example no net food or feed transfer across the watershed.

3.2. Catchment Nitrate Transport

[28] Groundwater flows through the Thames catchment are widely perceived to have a multidecadal mean travel time (MTT) due the decadal migration pathways through highly permeable unsaturated and saturated fractured rocks, composed mostly of chalk [*Howden et al.*, 2010]. Field investigation of these systems tends to highlight significant complexity in terms of field-scale and short-term processes [*Ireson et al.*, 2006; *Mathias et al.*, 2007a; *Butler et al.*, 2009]. Although much progress has been made concerning the simulation of such systems within conventional (Darcy's law, advection-dispersion equation, matrix diffusion, etc.) physically based-type models [*Mathias et al.*, 2006; *Ireson et al.*, 2009], parameter uncertainty and computational demand continue to render a detailed modeling approach impracticable for catchment-scale problems [*Jackson et al.*, 2006; *Mathias et al.*, 2007b]. We therefore used a modified model approach developed specifically for UK chalk catchments [*Howden et al.*, 2011b].

[29] The approach is limited to a simple lumping of all processes over the whole catchment, due a lack of spatial information to define inputs at a sub-basin scale over such a long period. Given past experience [e.g., *Mathias et al.*, 2007b], we deliberately sought a parsimonious model to identify key catchment-scale attenuation capacity, partitioning between runoff and groundwater pathways and long-term storage in the groundwater.

[30] The transport model calculated stream nitrate concentration, C_n, for the *n*-th year from:

$$C_n = C_b + \beta M, \tag{7}$$

where C_b is the baseline concentration in the river, β is a load-to-concentration conversion factor (a partition coefficient), and M is the load that contributes to fluvial concentrations in year n. M was estimated from:

$$M = \sum_{i=1}^{n} U_{n-i+1}\left[XB_{i(R)} + (1-X)B_{i(G)}\right] \tag{8}$$

for $n = 1, 2, \ldots n$, where U was a matrix of available nitrate for leaching in any given year, which was routed through either surface, $B_{i(R)}$ or groundwater, $B_{i(G)}$, controlled by the parameter X. The two reservoirs, (R) and (G), used the same formulation for B_i, thus:

$$B_1 = 0,\ B_n = A(t_n) - A(t_{n-1}),\ 2 \geq n \leq N, \tag{9}$$

which used a response function, $A(t)$, calculated as the analytical solution to the 1-D advection-dispersion equation for a slug injection at time $t = 0$:

$$A(t) = \frac{1}{2}\left\{\mathrm{erfc}\left[\left(1 - \frac{t}{t_a}\right)\sqrt{\frac{P_e t_a}{4t}}\right] + \exp\left[\frac{P_e}{2}\right]\mathrm{erfc}\left[\left(1 + \frac{t}{t_a}\right)\right]\sqrt{\frac{P_e t_a}{4t}}\right\},\ t \geq 0, \tag{10}$$

where P_e denoted the Peclet number and t_a was the mean travel time. Thus, two parameters were required to describe the transport through each reservoir. *Howden et al.* [2011b] noted that:

$$\lim_{P_e \to \infty}[A(t) = H(t - t_a)], \tag{11}$$

where H denoted the Heaviside step function. This suggests that, for high Peclet numbers, the model may be reduced in complexity to a simple time lag, removing the need to represent attenuation in the catchment system.

3.3. Nitrate Transport Optimization

[31] We used the median estimate of nitrate available for leaching in the catchment and a Monte Carlo approach to optimize the transport model parameters (X, $P_{e(R)}$, $P_{e(G)}$, $t_{a(G)}$, C_b, β) to predict the observed annual average fluvial nitrate concentrations, using an ensemble of 10^6 parameter sets. It was assumed the runoff was immediate, i.e., $t_{a(R)} = 0$; given the annual average nitrate concentrations in 1870, under some anthropogenic loading were $\sim$2 mg l^{-1}, we constrained the range of possible river baseline concentrations to be in the range $0 \leq C_b \leq 2$. Parameter β to convert nitrogen available for leaching into a river concentration was assumed in range of $0.01 \leq \beta \leq 0.05$; the maximum value was estimated from the quotient of the concentration range to loading range over the 140 years. The split between runoff and groundwater reservoirs was assumed to be similar to the surface-groundwater ratio in the river, estimated as 35% runoff and 75% groundwater for the Kingston flow gage; we therefore used $0.35 \leq X \leq 0.75$. Other parameter ranges are described in Table 2. The objective function to determine model fit to observed data was the mean average error (MAE); model optimization was considered 1.2×10^6 parameter sets.

4. Results

4.1. Long-term Changes in Thames Nitrate Concentration and Flux

[32] Figure 1 shows nitrate concentrations in the River Thames at Hampton since 1868. After an initial rise in the

Table 2. Parameter Ranges for Monte Carlo Optimization[a]

Parameter	Min	Max
X	0.3	0.7
$P_{e(R)}$	0.1	2000
$P_{e(G)}$	0.1	2000
$t_{a(G)}$	10	50
C_b	0	2
β	0.01	0.04

[a]These were selected based on an earlier application of the model [*Howden et al.*, 2011b] with the exception of partitioning between runoff (X) and groundwater flow ($1 - X$), which was set based on the published range of base flow estimates for the Thames.

1870s, concentrations remain relatively consistent until 1940. Nitrate concentrations rose during and after World War II (WWII) and then stabilized at almost double their previous level. There was a further step-change in the early 1970s, since when they have remained stubbornly high. *Howden et al.* [2010] showed that there had been no significant trend in flow over the period so that observed long-term changes in flux relate solely to long-term changes in concentration.

4.2. Sewage Contribution to Concentrations and Fluxes

[33] Figure 2 shows the proportion of net inputs from sewage and agriculture. The catchment population and related sewage inputs have risen steadily over the period. It is noticeable that the proportion of annual average nitrate concentrations contributed from nonsewage sources decreased linearly from the late 1970s to the early 2000s.

4.3. N Available for Leaching

[34] Biological fixation remained constant at 45 kg N ha^{-1} yr^{-1} (±10%). Atmospheric deposition was 5 kg N ha^{-1} yr^{-1} (±10%) prior to 1920, rising to 16 kg N ha^{-1} yr^{-1} (±25%) in 1970 and remaining constant thereafter. In both cases, the values used are taken from literature sources in the absence of catchment-specific observations.

[35] The predominant source of nitrogen prior to 1940 was from animal excretion, declining from 100 kg N ha^{-1} yr^{-1} to 60 kg N ha^{-1} yr^{-1} in 1940. In 1940, animal inputs increased rapidly back to the pre-1940 maximum of 100 kg N ha^{-1} yr^{-1} and remained at that level through to 2007. Inorganic fertilizers were of little importance prior to 1940. Between 1940 and the early 1980s, there was a rapid increase from around 20 kg N ha^{-1} yr^{-1} to 150 kg N ha^{-1} yr^{-1}since1980. Fertilizer inputs have gradually fallen since then but still remain around 110 kg N ha^{-1} yr^{-1} (Figure 3).

[36] The N release, because of plowing of permanent and temporary grassland, had little influence before World War I. Loads declined from 35 kg N ha^{-1} yr^{-1} in 1914 to 10 kg N ha^{-1} yr^{-1} in 1939. Widespread plowing of permanent grassland in the period 1940–42 caused a peak release of 100 kg N ha^{-1} yr^{-1} which slowly declined through to late 1990s to a level of ~20 kg N ha^{-1} yr^{-1} before further release in the late 1990s, which was associated with the end of set-aside schemes.

[37] Uptake by crops was estimated to decline from 100 kg N ha^{-1} yr^{-1} in 1870 to ~95 kg N ha^{-1} yr^{-1} in 1940; thereafter, it increased to 120 kg N ha^{-1} yr^{-1} and has remained relatively constant to the present. Uptake by both permanent and temporary grassland was estimated to be less than 20 kg N ha^{-1} yr^{-1} throughout the entire period. At no time were there temporary or permanent grasslands net accumulators of nitrogen (Figure 3).

[38] The total N available for leaching (Figure 3e) varied from ~50 kg N ha^{-1} yr^{-1} in the late 1860s, which gradually fell to ~30 kg N ha^{-1} yr^{-1} by 1940, except for a short rise in 1918–19 caused by plowing of pasture during the First World War (WWI). There is a rapid rise to 150 kg N ha^{-1} yr^{-1} in 1940 because of the plowing of permanent grassland, which falls to ~100 kg N ha^{-1} yr^{-1} by the late 1950s, before rising

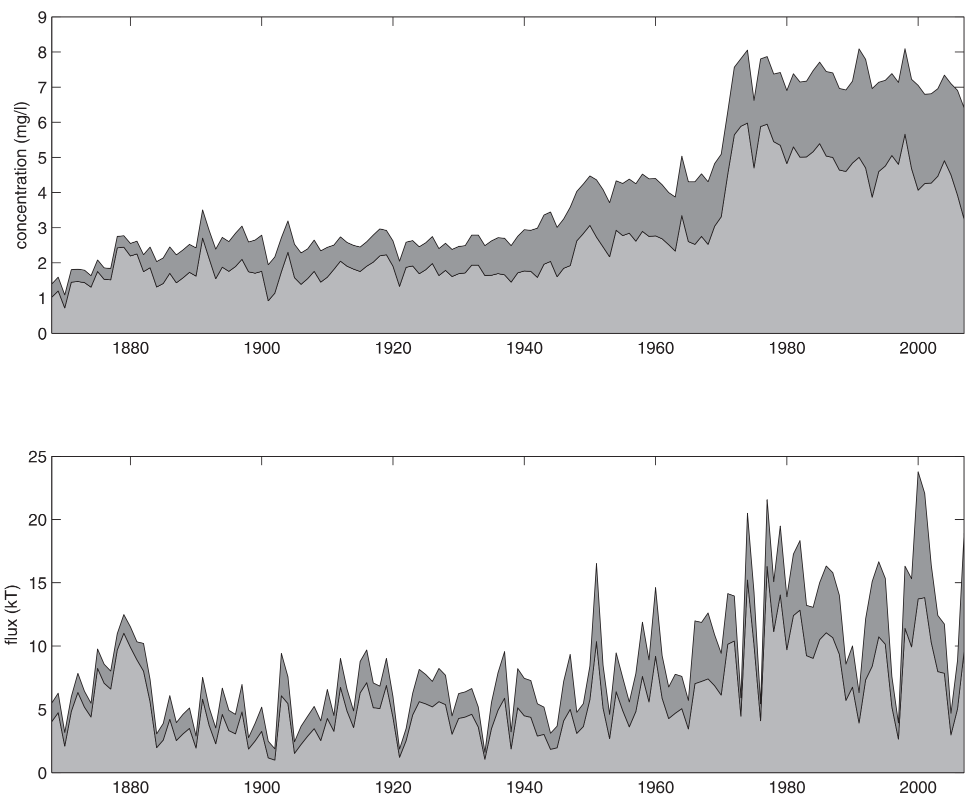

Figure 2. The contribution of agricultural and sewage effluent sources to nitrate concentrations in the River Thames.

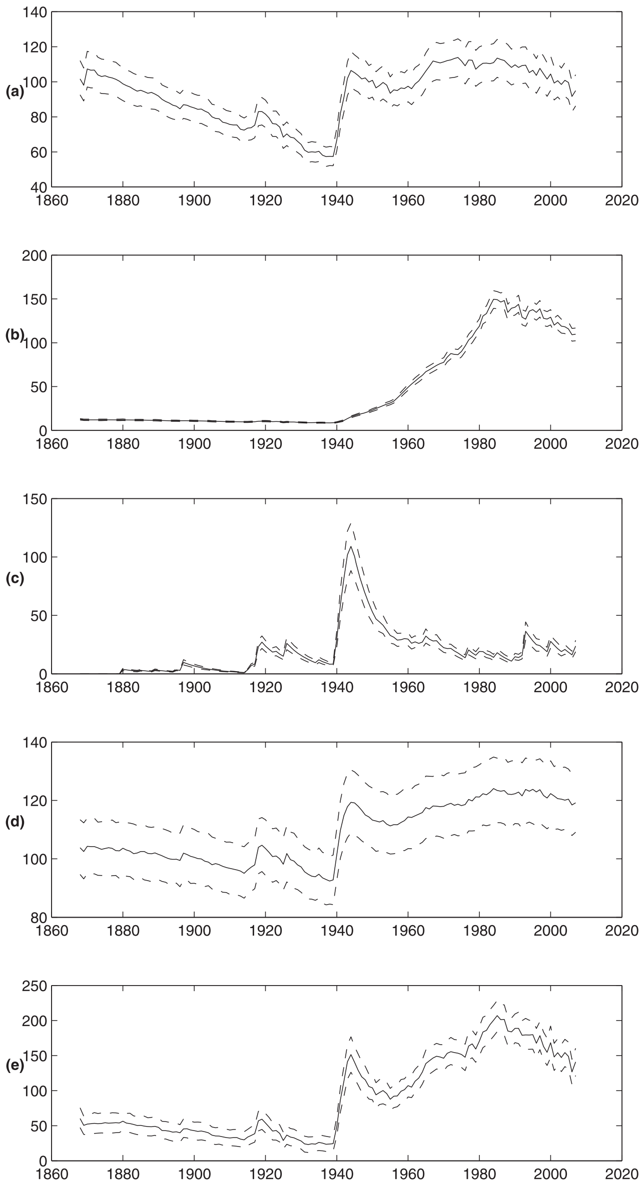

Figure 3. Estimated loading components: (a) animal inputs; (b) fertilizer inputs; (c) inputs from enhanced mineralization because of plowing of permanent grassland; (d) losses from uptake from crops and grasslands; and (e) estimated nitrogen available for leaching. The plots were generated from ensembles of 1001 estimates of each input component, summarized to show median, 5th, and 95th percentiles of estimated inputs.

steadily to almost 200 kg N ha^{-1} yr^{-1} by the mid 1980s. After this, the N available for leaching decreases to 150 kg N ha^{-1} yr^{-1} by 2008.

4.4. Catchment Nitrate Transport Model: Parameters and Optimization

[39] The catchment nitrate transport model was used to convert the median estimated annual load into streamflow concentrations (Figure 4) and allowed for two flow pathways: one immediate and the other delayed by up to 50 yrs (t_G), the proportional split for the runoff pathway (X) assumed to be between 35% and 75% ($1 - X$ for groundwater). Each flow pathway allowed some attenuation ($P_{e(R)}$, $P_{e(G)}$). The in-stream effect of catchment N loading assumed the river baseline concentration (C_b) increased in proportion to the transported load according to a factor (β), which is effectively a partition coefficient.

[40] Model optimization showed the optimal delay was between 30 and 31 yrs (Figure 5), which is also evident from a comparison of Figure 3e and Figure 2a: the large step change in loading in the years 1940–1945 was followed by a large step change in concentrations in 1970. Model performance improved as attenuation in the two flow pathways increased, suggesting a linear translation of input to output, albeit delayed for three decades in the case of groundwater.

[41] The published base flow index (BFI) for the River Thames of 64% (http://www.ceh.ac.uk/data/nrfa/data/spatial.html?39001) suggests a dominant contribution of groundwater. However, our model optimization suggests surface contributions of between 50% and 60% from the surface runoff pathway. BFI is estimated from areas of bedrock geology, rather than an analysis of river flows, so this is not entirely surprising. River baseline concentrations are estimated to be between 0.8 and 1 mg NO_{3^-} N l^{-1}. Given the influence of sewage inputs was already accounted for, this range of values represents a preindustrial natural background concentration, which is consistent with measurements of other pristine UK water sources from similar terrain and geology [*Limbrick*, 2003; *Howden and Burt*, 2008, 2009].

[42] Figure 5 shows a matrix plot of the top 10% performing parameter sets (1.2×10^5 sets). It is clear that the optimal model fits occupy a defined area of the parameter space, and several similar parameter sets represent equally good models. The median prediction from the top 1.2×10^4 model fits is shown in Figure 5. Overall, the model fit is good with an overall mean absolute error (MAE) of just over 0.4 mg l^{-1}. There are three periods when the model does not manage to reproduce the observed data: 1868–1880, 1940–1945, and 1970–1983. Pre-1880, there is little consistency in observed nitrate concentrations, ascribed to the relatively new chemical methods being used. From 1881, independent observers verified the observations; we can therefore have more confidence in observations after that time. It is, however, surprising that the model predicts a much more rapid response after 1940 than is evident in the data. Finally, the model captures the rapid rise in concentrations at the end of the 1960s, due to the delay in inputs from WWII, but it does not fully capture the peak concentrations in the late 1970s. This is not entirely surprising as the model makes no allowance for the influence of wet or dry periods on nitrate concentrations, and the peak values may, in part, relate to post-1976 drought effects [*Foster and Walling*, 1978].

4.5. Cumulative N Storage

[43] Figure 6 a shows the accumulation of N in the catchment as the difference in estimated inputs and observed output, assuming nitrate is the major form of N in output (the national average is 65% of the total fluvial N flux [*Worrall et al.*, 2009b]). The apparent accumulation before 1940 (~35 [±15] kt N yr^{-1}) relates to unaccounted

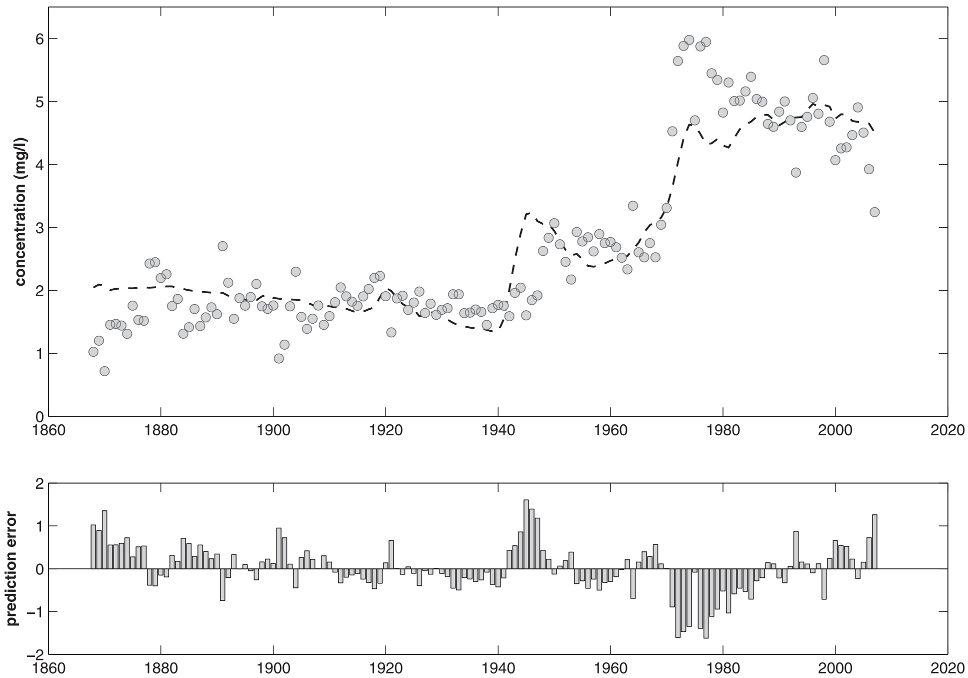

Figure 4. Median predictions from the 12,000 top-performing parameter sets predicting nitrate concentrations in the Thames, from 1868 to 2008.

losses and especially in-stream losses via utliziation and denitrification. Assuming steady state before 1940 (i.e., no net change in catchment N storage), then the accumulation rate prior to 1940 can be taken to represent as these previously unaccounted for losses. Figure 6b shows the effect of removing the unaccounted losses (at a rate equivalent to that estimated for pre-1940) across the whole period. The results suggest that there is an accumulation of N in the catchment from 1940 onward and that, moreover, there has been very little decline in the rate of accumulation in recent years. *Worrall et al.* [2009b] estimated that the UK was a net sink for reactive nitrogen (N_r [*Galloway et al.*, 2004]) of at least 420 kt N yr^{-1} (i.e., inputs exceed fluvial outputs), although the value of the sink had declined at an average rate of 32 kt N yr^{-1} since 1992. We use the term "sink" to suggest either a net accumulation of nitrogen or an unidentified loss of reactive nitrogen. If this rate is applied to the Thames then we could assume an accumulation rate of 17 kt N yr^{-1}, whereas Figure 6b suggests an accumulation rate of 100 k N yr^{-1}. Reactive N sinks have also been observed for other developed countries (e.g., Netherlands [*Kroeze et al.*, 2003]). Some of this storage may be accounted for, given the catchment transport model identified ~50% of leached N travels to the stream via a groundwater pathway with an ~30-yr travel time. However, it is notable that there does not appear to be any reduction in the size of the N sink in the Thames basin.

4.6. Scenarios of Input Reduction

[44] Using the optimized model parameters, we ran two scenarios to consider the potential effect of reducing fertilizer usage over the past 140 yrs. Two scenarios, shown in Figure 7, were considered: a reduction of 50% and 100% in fertilizer inputs, respectively. It is clear that such dramatic reductions in fertilizer inputs would not have completely removed the nitrate problem, concentrations would have remained below an annual average of 3 mg l^{-1} before 1975, and between 1975 and 2008, would have steadily decreased to ~2 mg L^{-1}.

5. Discussion

[45] It is difficult to model the impact of changes in nutrient loading on surface and groundwaters over long timescales because it remains unclear how best to represent basin-scale solute transport through soil, unsaturated, and saturated zones [*Mathias*, 2005]. Notwithstanding this, there is an urgent need for water resource scientists to develop new model approaches, improve conceptual and perceptual understanding of surface and groundwater processes, and the underlying time-constants that dictate their response to forcing. At the same time, the challenge of prescribing sustainable practices to ensure a consistent supply of essential ecosystem services (e.g., food production, water supply, and ecological quality) remains daunting.

[46] In this paper we presented a simple catchment model to quantify N inputs to the Thames basin over 140 yrs, and together with a record of observed nitrate concentrations in the river, built a simple model to estimate how N applied to land via agricultural practices was routed through surface and groundwater systems to the basin outfall. The basin was represented by a small number of discrete, spatially lumped stores, which represent a limited number of mean residence times. Although the importance of representing the chalk unsaturated zone response is well established [*Oakes et al.*, 1981], understanding how to achieve this in a simplified manner, appropriate for conceptual models, is not [*Mathias*, 2005; *Jackson et al.*, 2006]. Even though the water table can

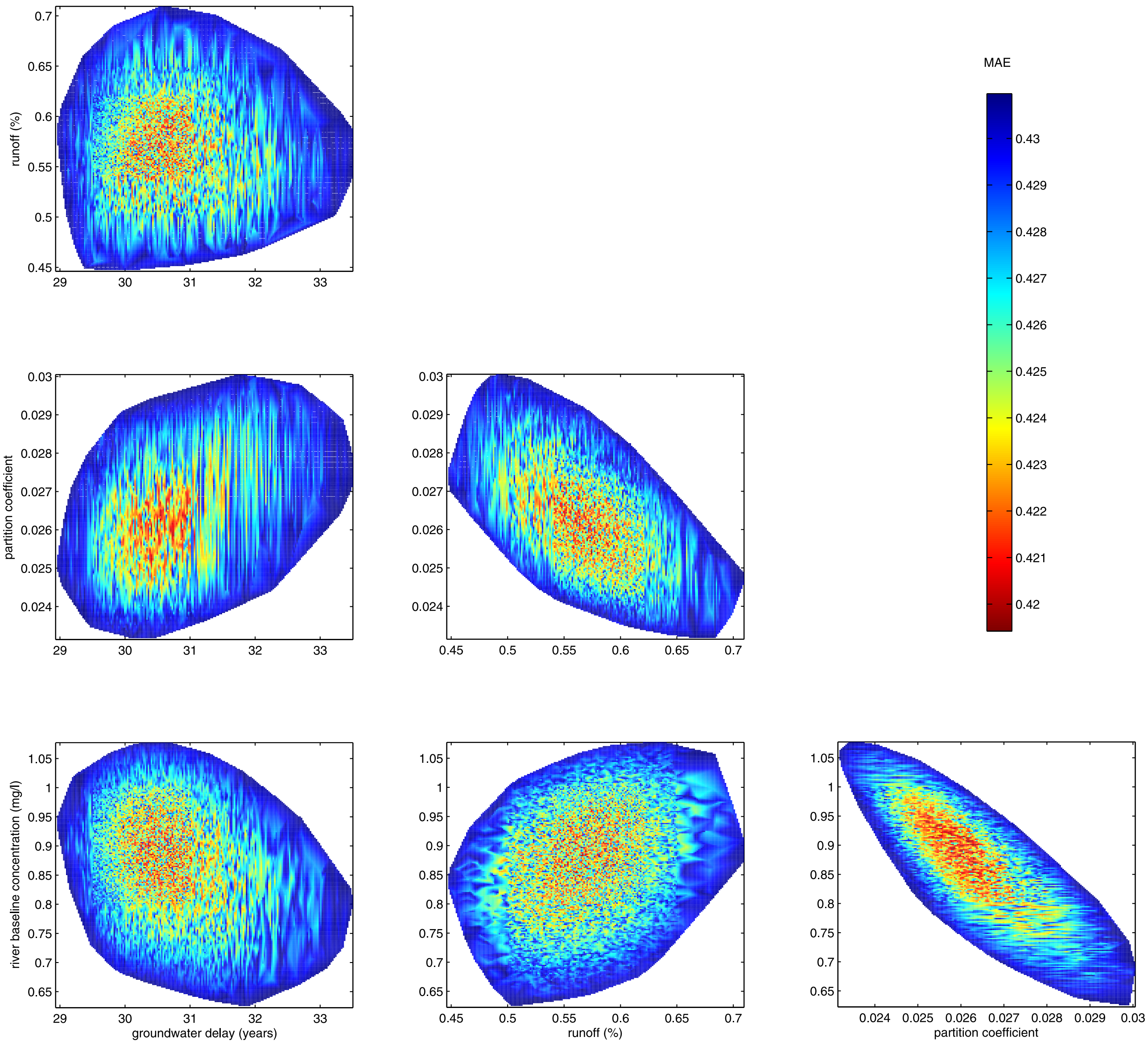

Figure 5. Amatrix plot of model optimization results showing the best 10% of models (120,000 of 1.2 $\times$ 10^6).

respond rapidly (of the order of days) to major infiltration episodes, the extremely damped nitrate response (of the order of decades) suggests that the water is of varying residence time, much of it taking a very long time to reach the river [*Jackson et al.*, 2006]. In a large catchment like the Thames, there is more than one aquifer in any case, which introduces an added complication in how to structure the model. The problem becomes even more complex [*Tetzlaff et al.*, 2008; *Howden et al.*, 2011b] when the history of nutrient loading is considered. Current catchment-scale conceptual models are unable to represent the history of loading, in part, due to the limited number of travel paths they represent, but also because the very long timescales involved mean that relevant data on river water quality and local drivers are often not available for the whole period. There are therefore at least two major elements of epistemic uncertainty in modeling long-term solute transport in groundwater-dominated river catchments [*Howden et al.*, 2011b]: uncertainty in inputs, model sensitivity to these uncertainties, and, uncertainties related to model structure and parameterization. All of this limits the mobility of any model; an acceptable model for one catchment cannot necessarily be transferred to a new site.

[47] Notwithstanding these complexities and the identified uncertainties, there is an urgent need to improve understanding of river catchment systems such that land managers can ensure the externalities of agricultural production are kept to an acceptable level.

[48] The uniquely long records for land use and water chemistry in the River Thames catchment provide an opportunity to experiment with new modeling approaches that seek to answer some fundamental questions about the role of runoff and groundwaters in transporting nitrate from the land to water resources. The time delays are inherent in either pathway, as well as any indications of what pristine baseline conditions, or natural attenuation/denitrification capacity of the catchment might be.

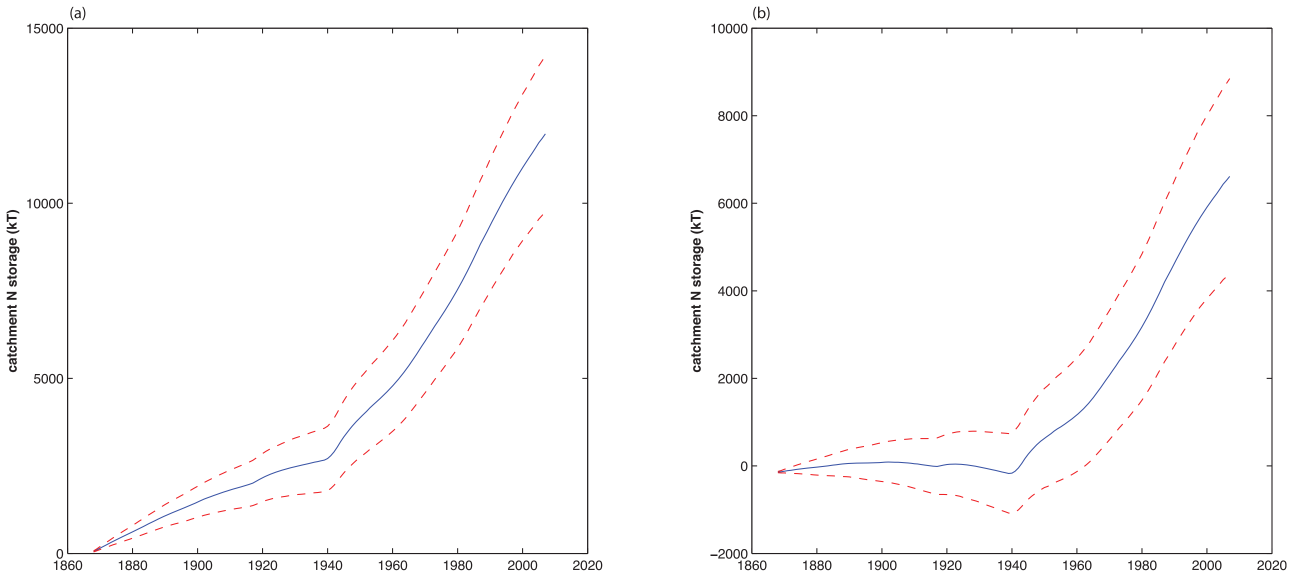

Figure 6. Net accumulation of nitrogen in the Thames catchment between 1880 and 2008. Dotted lines indicate the range of estimates for nitrate leaching availability. 6a Shows the raw accumulation over time; 6b shows the excess accumulation since 1940 assuming the pre-1940 removal is representative of catchment-scale capacity for denitrification and in-stream removal.

[49] The challenge for watershed hydrologists is to produce models that are sufficiently sophisticated to capture high-level process understanding, while also being useful to inform practical decision-support for land managers. The modeling approach outlined in this paper seeks to make that compromise, using a parsimonious model structure to provide estimates of water resource status at the catchment scale. Clearly, there are limitations to the model presented:

[50] 1. There is no recognition of spatial variability across the catchment. This is largely a constraint of the land-use summary data, which are given for the Thames catchment as a whole. Of course, a spatially explicit model is highly desirable, but it not entirely necessary in the context of outlining an input-output balance. The model is intended to provide an inference of processes occurring at the catchment scale.

[51] 2. The model only considers an annual time step. Again, this is a constraint of available land use data. However, in the context of this study, we are interested in the long-term, not the short-term and, therefore, we argue that an annual time step is sufficient for this purpose.

[52] 3. There are many detailed processes that control groundwater movement that have not been considered in the model. *Howden et al.* [2011b] recently showed the epistemic uncertainties in understanding these processes, demonstrating that the pattern of historical N loading water is

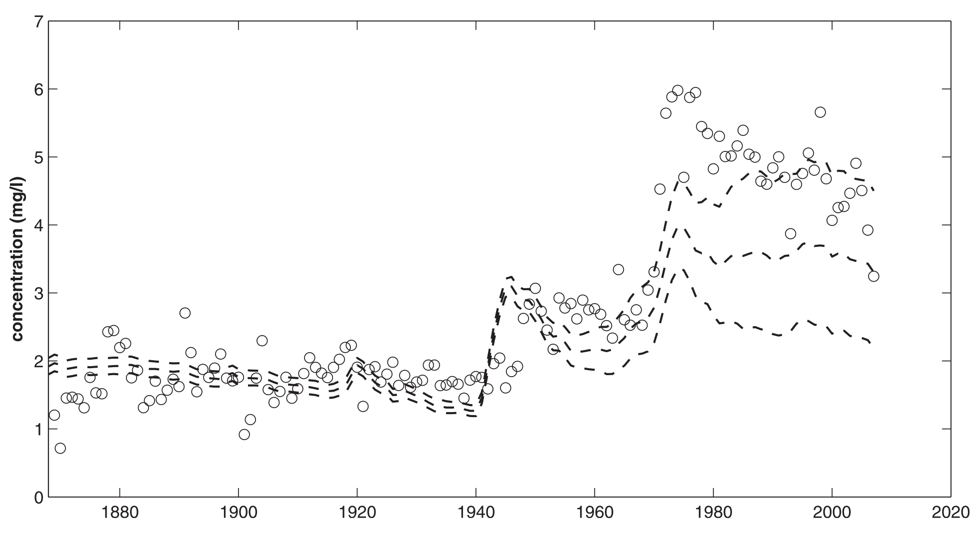

Figure 7. Annual average nitrate concentrations in the Thames north of London at Hampton, from 1868 to 2008 (corrected for sewage inputs) with the model fit based on estimated actual loading and two further scenarios: historical fertilizer loading reduced by 50% and then 100%, respectively.

much more important in determining freshwater nitrate concentrations than these complex transport mechanisms. In fact, the transport mechanisms were more adequately represented by the very simple model structure presented here than by a complex spatially explicit model of the aquifer.

[53] It is notable that the two-reservoir model is largely insensitive to changes in the attenuation parameters, in fact, the only sensitivity identified was a notable improvement when the Peclet numbers were increased toward infinity. This suggests that the nitrate available for leaching in any given year is removed immediately to the river system, or is transported through the groundwater to reach the river ~30–31 yrs later. For many years, it was assumed that the rapid increase in nitrate concentrations in the River Thames between 1968 and 1972 was due to the agricultural intensification during the 1960s. However, our model suggests this is not true; the two step-changes in nitrate concentration observed in the Thames record occur because of the step-change of nitrate available for leaching at the start of WWII. This is initially because of the plowing of permanent grassland. As this effect reduces through the 1950s and 1960s, the nitrate available for leaching due to fertilizer inputs and intensification increases, thus maintaining the step-change started in 1940. Therefore, the effect of intensification was to maintain leaching levels, rather than to increase them.

[54] The conclusion from this analysis is, therefore, that the large jump in nitrate concentrations from 1968 to 1972 is entirely due to a groundwater response to plowing during WWII. This raises the following questions in the context of the sustainable use of the catchment for agriculture: How will past agricultural impacts continue to influence ambient conditions?; What constraints does this place on food production in coming decades?; and Over what timescale must we implement management plans to return agricultural catchments to a more sustainable position? The results presented here raise questions about what exactly "sustainability" means in the context of groundwater resources. In the Thames basin, this could relate to both quantity and quality, although we have only considered the latter here. In relation to water quality, there are major uncertainties associated with the long timescales of response, both in relation to what future nitrate concentrations might be and how quickly they might respond to significant land use change.

[55] The study predicts that the Thames is, and has been for at least 60 yrs, a net sink of reactive nitrogen, as observed in other developed agricultural countries [*Parris*, 1998], but where is this nitrogen going? This nitrogen could be stored in the terrestrial biosphere in land not currently used for food production, but this is unlikely as there is little such land in the intensively farmed Thames basin. If anything, such a land area would have declined over time with progressive intensification. The nitrogen could be stored in the subsoils, i.e., in the part of the profile less affected by plowing or land use change. But this would imply carbon storage could also be increasing and there is no evidence of this additional carbon sequestration [*Bellamy et al.*, 2005]. Further, this study has not considered the change in storage in groundwater and surface waters. A 1 mg N/L rise in groundwater nitrate concentration since 1990 was observed in the UK by *Stuart et al.* [2007]. If we consider that significant groundwater bodies cover 50% of the Thames catchment and that this groundwater body represents an equivalent depth of water of up to 10 m then a 1 mg N L^{-1} yr^{-1} increase in average groundwater concentration would represent an additional 5 kt N of storage per year within the catchment. Further, this would be storage in the saturated zone of the aquifers, and we could therefore consider an equivalent storage in the unsaturated part of aquifer. The capacity for nitrogen removal within aquifers is often very low, typically <1% of predicted annual input [*Hiscock et al.*, 2003], and so the increase in nitrate in the aquifers below the soil profile does represent a significant store of reactive nitrogen and so does indeed constitute a "time bomb," i.e., it will come out eventually and perhaps suggests we have yet to see the worst of the nitrate pollution.

6. Conclusions

[56] The very long record of nitrate concentrations for the Thames at Hampton from 1868 provide the basis for modeling nitrate export from the Thames basin. The nitrogen available for leaching from agricultural land was estimated using a combination of land-use records and values taken from the literature. Population data were used to estimate inputs to the river from sewage. A two-reservoir routing model was used to calculate stream nitrate concentrations. Model optimization showed the optimal delay was between 30 and 31 yrs with ~40% to 50% of river discharge having passed through the delayed groundwater store. The model results suggest that advection is the dominant mechanism for groundwater flow in the Thames basin; there is little or no dispersion present. In presenting a lumped model with an annual time step, we are aware that many important process mechanisms have been explicitly ignored, but argue that the advantages of a relatively simple model outweigh the disadvantages.

[57] The estimates of historical nitrogen loading to the Thames catchment, derived from land-use and management records, suggest that catchment N loading has increased by a factor of up to 3 since the 1930s. This was principally because of enhanced N mineralization following plowing of permanent grasslands during World War II. Only relatively recently have fertilizer inputs to land become the dominant source of leachable nitrate.

[58] Model results suggest that that there has been significant accumulation of nitrogen in the catchment from 1940 onward and that, moreover, there has been very little decline in the rate of accumulation in recent years. Some of this apparent accumulation could, in fact, have been lost by enhanced denitrification in response to higher nitrogen loadings but that apart, the implication is that the Thames aquifers have become major stores of nitrate in recent decades. Given a time lag of 30–31 yrs for movement of nitrate through the aquifers of the Thames basin, the results suggest that any reduction in nitrate concentrations of river water and groundwater, following significant change in land management practices, will take several decades to take effect. Such timescales of response are well beyond those of political cycles showing that any solution to the nitrate issue will require a long-term vision for water-quality remediation, similar to those adopted within the EU's Water Framework Directive. In terms of sustainable groundwater, there seem to be no "quick fixes" [*Burt*, 1994]. Moreover, if groundwater nitrate concentrations are indeed continuing to rise in the

UK [*Stuart et al.*, 2007], then the worst may be yet to come, a gloomy prospect for water-quality management in groundwater-dominated river basins.

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